On the Control of the porosity of different activated carbons by chemical activation of sodium lignosulfonate

Miguel García-Rollán, Ramiro Ruiz-Rosas, Juana María Rosas, José Rodríguez-Mirasol, Tomás Cordero

Universidad de Málaga, Andalucía Tech, Departamento de Ingeniería Química, 29010, Málaga, España

Objective:
The valorization of lignin for the production of activated carbons by chemical activation with phosphoric acid.

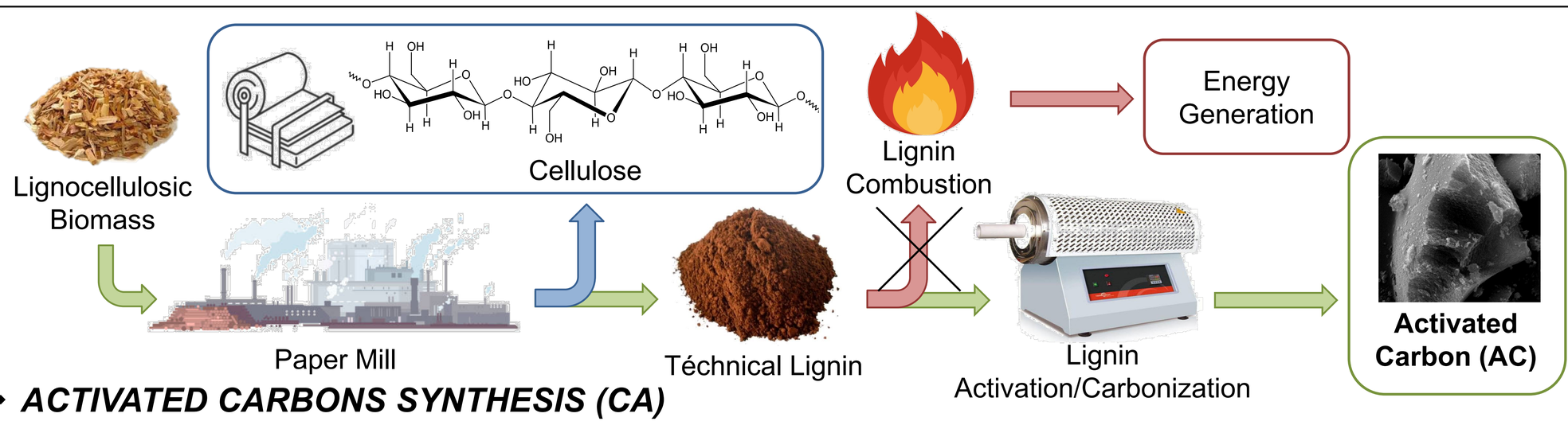
The chemical activation of three lignin-based precursors (sodium lignosulphonate as received, thermal treated lignin, thermal treated-acid washing lignin) was studied at different impregnations ratios and activation temperatures.

High solubility of LS in the activation media (85% H_3PO_4 aqueous solution), allows the production of ACs with high micropore volume and a wide mesoporosity. The use of impregnation ratios of 3:1 increases the mesopore volume up to V_{mes} 1.86 cm^3/g. As for the activation temperature, for high impregnation ratios, temperatures above 500 ºC must be reached for a higher development of the wide mesopore, at the cost of a small decrease of micropores. Above 700 ºC, the carbon structure is rearranged and the porosity shrinkage is observed.

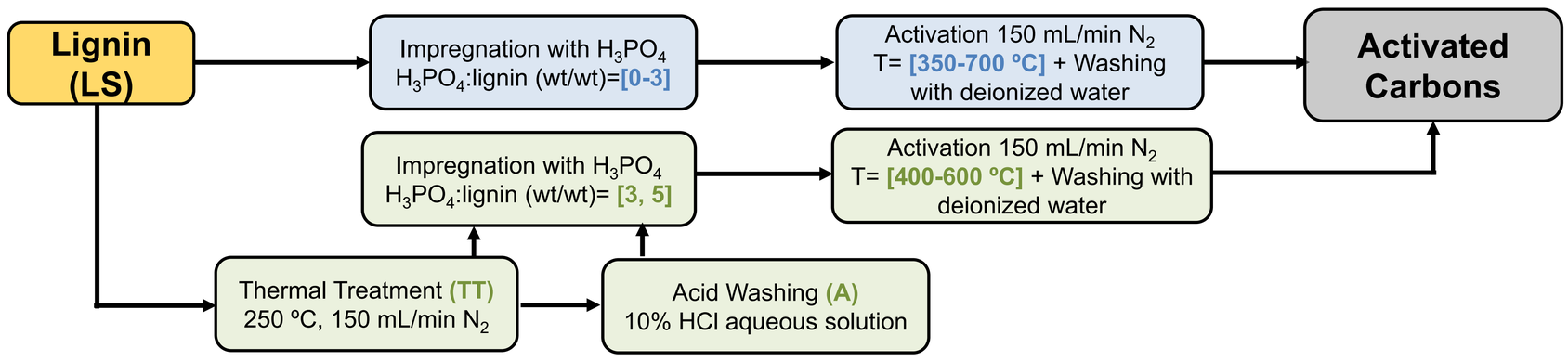
The thermal treatment (TT) seems to produce a transformation of the inorganic sulfur species in the LS. The acid washing (A) modify the surface chemistry of the material releasing carbonates and generating CO-evolving groups.

The chemical activation of the LSTT precursor produces an AC with a lower pore development than that obtained by chemical activation of the raw material (LS). However, after the acid-washing (A) process, the chemical activation produces AC with the largest micropore development (Vs up to 1.08 cm^3/g).

❖ INTRODUCTION



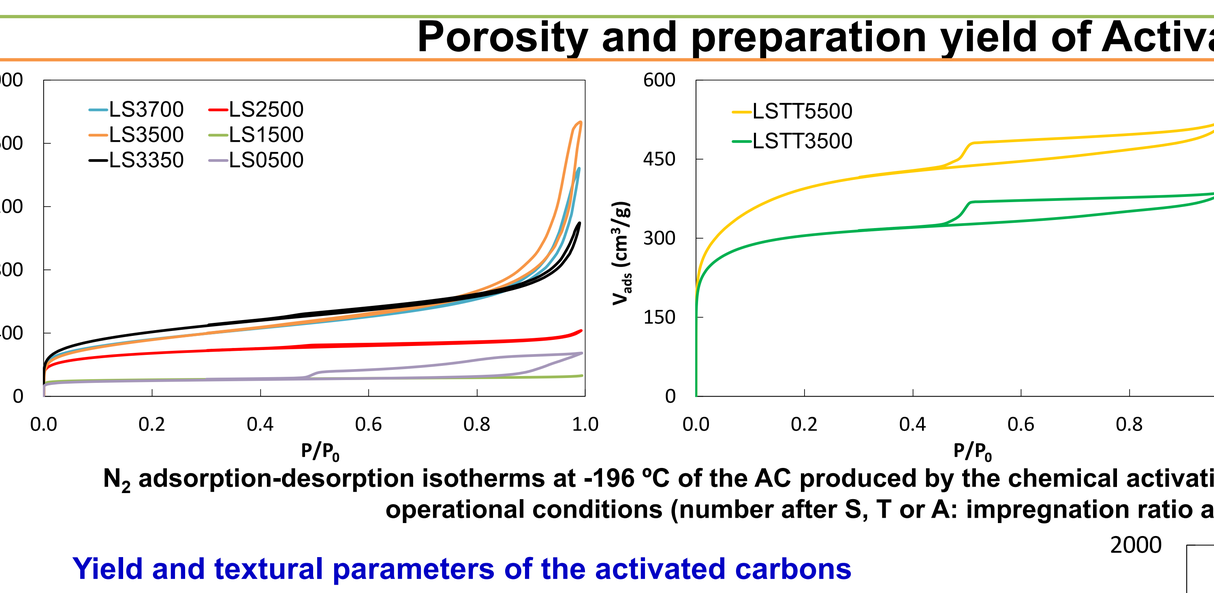
❖ ACTIVATED CARBONS SYNTHESIS (CA)



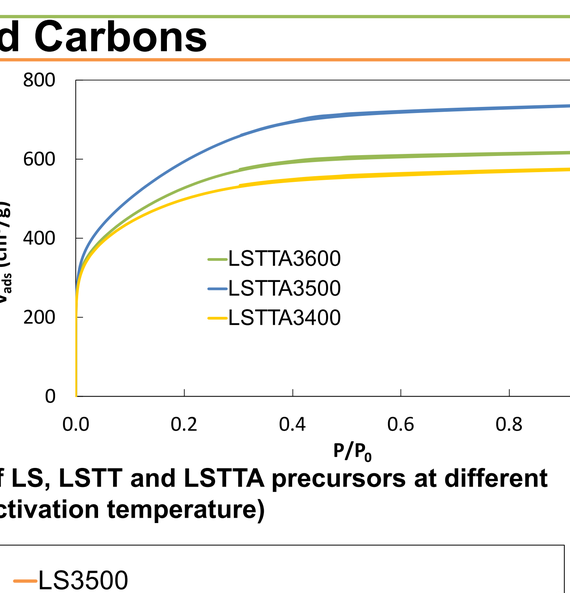
❖ CHARACTERIZATION

Surface chemistry and chemical composition of activated carbon precursors

Sodium Lignosulfonate= **LS**; Lignin Thermal Treated= **LSTT**; Lignin Thermal Treated and Acid Washed=**LSTTA**



CO and CO_2 evolution during a thermal treatment of the carbonaceous precursors



Evolution of sulfur compounds during a thermal treatment of the carbonaceous precursors

a) The thermal Treatment at 250 ºC reduced the cleavage of less stable bonds that evolve as CO_2.
b) The acid washing reduced the evolution of CO_2 and CO at high temperature, which seems to be related to the removal of the inorganic matt (XPS and ash content).
c) The thermal treatment of lignin at 250 ºC seems to transform sulphone groups into thiols (evolution of SO_2 is replaced by evolution of H_2S at higher temperatures).

Ultimate analysis and surface chemical composition measured

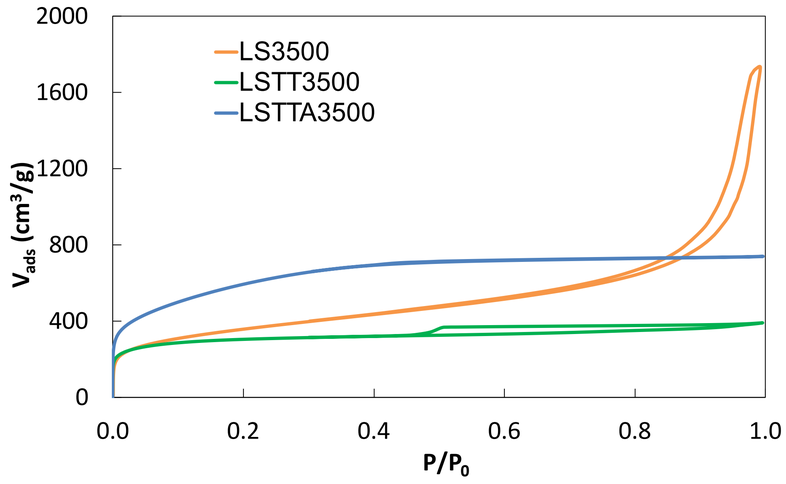
Samples	Ultimate Analysis C (%)	H (%)	N (%)	S (%)	Ash Cont. (%)	XPS C (wt%)	O (wt%)	S (wt%)	Na (wt%)
LS	33.2	4.4	0.2	3.8	16.9	51.1	32.1	6.9	9.9
LSTT	37.5	3.4	0.1	3.9	24.1	25.4	38.2	1.6	34.8
LSTTA	54.2	4.1	0.2	5.5	1.5	68.6	25.8	4.4	1.2

Porosity and preparation yield of Activated Carbons

N_2 adsorption-desorption isotherms at -196 ºC of the AC produced by the chemical activation of LS, LSTT and LSTTA precursors at different operational conditions (number after S, T or A: impregnation ratio and activation temperature)

Yield and textural parameters of the activated carbons

Samples	Yield (%)	N_2 Adsorption A_{BET} (m^2/g)	V_{mes} (cm^3/g)	V_s (cm^3/g)	A_S (m^2/g)	CO_2 Adsorption A_{DR} (m^2/g)	V_{DR} (cm^3/g)
LS0500	28.4	375	0.26	0.13	55	370	0.15
LS1500	35.5	395	0.02	0.16	10	420	0.17
LS2500	31.3	1000	0.18	0.43	100	535	0.21
LS3350	31.6	1480	1.00	0.54	445	545	0.22
LS3500	**34.7**	**1290**	**1.86**	**0.37**	**620**	**470**	**0.19**
LS3700	28.7	1255	1.60	0.39	560	580	0.23
LSTT3500	**23.5**	**1160**	**0.15**	**0.45**	**95**	**640**	**0.26**
LSTT5500	18.4	1450	0.20	0.61	120	620	0.25
LSTTA3400	19.0	1805	0.06	0.83	50	750	0.30
LSTTA3500	**19.0**	**2175**	**0.07**	**1.08**	**50**	**755**	**0.30**
LSTTA3600	18.9	1905	0.05	0.91	40	810	0.32



Comparison of N_2 adsorption-desorption isotherms at -196 ºC of the ACs of LS, LSTT and LSTTA activated at the same operational conditions.

Acknowledgments: The authors acknowledge the support from Spanish Science, Innovation and Universities Ministry (RTI2018-097555-B-I00), by Junta de Andalucía (UMA18-FEDERJA-110 and P18-RT-4592) and in addition, M.G.R. acknowledges the assistance of the same Ministry for the award of an FPU Grant [FPU 18/01402].